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(21) International Application Number: PCT/NL99/00328 (22) International Filing Date: 26 May 1999 (26.05.99) (30) Priority Data: 1009258 26 May 1998 (26.05.98) NL (71) Applicant (for all designated States except US): DELFT UNIVERSITY OF TECHNOLOGY, FACULTY OF CHEMICAL ENGINEERING AND MATERIAL SCIENCE [NL/NL]; Rotterdamseweg 137, P.O. Box 5025, NL-2600 GA Delft (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): BRINKMAN, Hendrik-Johan [NL/NL]; Trompetstraat 75, NL-2611 KM Delft (NL). DUSZCZYK, Jerry [NL/NL]; Zaaihoek 18, NL-2614 WX Delft (NL). KATGERMAN, Laurens [NL/NL]; Ch. Salomonlaan 2, NL-2642 CT Pijnacker (NL). (74) Agent: ALTENBURG, Bernardus, Stephanus, Franciscus; Octrooibureau Los En Stijger B.V., Weteringschans 96, NL-1017 XS Amsterdam (NL).		(81) Designated States: BR, CA, IN, NO, US, ZA, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Dutch).</i>
(54) Title: METHOD OF PREPARING AN Al-Ti-B GRAIN REFINER FOR ALUMINIUM-COMPRISING PRODUCTS, AND A METHOD OF CASTING ALUMINIUM PRODUCTS (57) Abstract <p>The invention relates to a method of preparing an Al-Ti-B grain refiner for cast aluminium-comprising products. According to the invention the preparation is realized by mixing powders selected from the group comprising aluminium, titanium, boron, and alloys and intermetallic compounds thereof, compressing, heating in an inert environment until an exothermic reaction is initiated and cooling. It has been shown that when the grain refiner thus prepared is applied, the quality of cast products remains substantially constant even during lengthy casting processes. The invention also relates to a method of casting aluminium products.</p>		

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Method of preparing an Al-Ti-B grain refiner for aluminium-comprising products, and a method of casting aluminium products

The present invention relates to a method of preparing an Al-Ti-B grain refiner for cast aluminium-comprising products, which grain refiner is prepared by:

- i) mixing powders selected from the group comprising aluminium, titanium, boron, and alloys and intermetallic compounds thereof;
- ii) compressing the mixed powders;
- iii) heating the compressed mixture; and
- iv) cooling the thus prepared grain refiner.

Such a method is disclosed in GB 2,299,099. According to this method the powders are compressed and sintered in order to provide a grain refiner that is easy to handle by both producer and buyer. Grain refining relates to the reduction of crystalline aluminium grains developing during solidification of aluminium in the aluminium melt. A small grain size is accompanied by a number of favourable properties; particularly the ductility and strength are improved. In addition, castability (during flow-casting) and extrudability are improved. With regard to sintering, mention is made in GB 2,299,099 that it can be used to achieve chemical changes. However, this is not considered to be necessary because these reactions will take place in the aluminium melt, if the grain refiner is used.

It is the object of the present invention to improve the method and in particular to provide a method providing an improved grain refiner. A more particular object of the invention is to provide a grain refiner having the property that by introducing the grain refiner into an aluminium melt, the grain size and consequently the quality of aluminium products produced from the melt remains constant, even if the melt is left to stand for a long time. This means that, for example, when during manufacturing aluminium products the container of the aluminium melt is emptied only slowly, the micro-structure of

products that are cast later on, will substantially be the same as of the products that were cast earlier.

To this end the method according to the present invention is characterized in that the compressed mixture
5 is heated in an inert environment to initiate an exothermic reaction.

Surprisingly, the property of the grain refiner thus prepared is such that during lengthy casting processes the quality of cast products remains substantially
10 constant. Heating initiates an exothermic reaction. This causes a temperature excursion in the compressed mixture inducing the development of a liquid phase which greatly promotes the movement of reactants. In this manner the starting products will to a large extent yield the desirable
15 final product with a high Al_3Ti and TiB_2 content. Due to the difference with the ambient temperature, the big rise in temperature is automatically followed by a strong cooling, which is also believed to contribute to the favourable properties of the grain refiner according to
20 the present invention.

In the present application, an inert environment is understood to be an inert atmosphere formed, for instance, by an inert gas such as a noble gas, or a vacuum.

The American patent specification 4,710,348 relates
25 to the manufacture of metal-ceramic composites. This publication contains a casual remark that a rod made from such a non-reacted mixture could be used as grain refiner for aluminium. When the rod is added to an aluminium melt, the constituent components of the mixture react to form
30 seeds, with the aid of which (aluminium) grain refining may be achieved. In other words, the grain refiner itself is prepared in situ (with the method according to the invention this occurs ex situ). Applicant has attempted to verify this suggestion experimentally, but has not
35 succeeded in achieving grain refinement.

According to another known method of the prior art, titanium- and boron-containing salts such as K_2TiF_6 and KBF_4 , are added to the molten aluminium having a temperature of 800-900°C. The salts decompose and titanium

and boron are taken up in the aluminium forming Al_3Ti and TiB_2 , comprised in an aluminium matrix. In EP 0,521,580 mention is made of this reaction being exothermic and difficult to control. In addition, the use of fluorides has the disadvantage that undesirable byproducts are formed, such as slag on the molten aluminium and gaseous boron fluoride. The latter is for environmental and health reasons undesirable. In addition, titanium and boron must only be added in limited amounts, as otherwise the viscosity of slag and the molten aluminium increase to such an extent that they can no longer be easily separated. This means that the grain refiner may only contain a maximum of 5% by weight of titanium and 1% by weight of boron, the rest comprising aluminium matrix.

According to a very favourable embodiment, the reaction parameters are adjusted such that the ratio of elongated and cubic Al_3Ti crystals is as low as possible.

Despite many years of research, the manner in which grain refiners work is not completely understood. Surprisingly, applicant has found that it is in particular the cubic Al_3Ti crystals that contribute to a further grain refinement and that it is possible to alter the ratio between elongated and cubic Al_3Ti crystals. This finding may contribute to a better understanding of the effect of grain refiners.

According to a favourable embodiment, the ratio is changed by choosing the mole ratio of B/Ti such that it is lower than 1.9, and in particular lower than 1.7, and more preferably lower than 1.5.

Preferably the size of the powders used in step i) is less than 100 μm .

This allows a highly elevated temperature to be reached with quick cooling. At the same time, Al_3Ti and TiB_2 are distributed more homogeneously in the aluminium matrix.

With respect to the contents, it is remarked that the mixture from step i) preferably comprises titanium in an amount of at least 10% by weight and more preferably at least 25% by weight.

The mixture from step i) further preferably comprises boron in an amount of at least 3% by weight and more preferably at least 5% by weight.

- 4 In this way a good grain refiner can be prepared.
5 If the percentages of titanium are lower, it is preferred that the percentage of boron be higher.

According to a favourable embodiment of the preparation of the grain refiner, AlB_{12} is used as the boron source.

- 10 AlB_{12} is known to have an unfavourable effect on the quality of cast products, in particular foils. By not reacting the reactants in situ (i.e. in an aluminium melt), and due to the fact that in the method according to the invention, AlB_{12} completely disappears during reaction,
15 it is surprisingly enough possible to prepare in a simple manner an excellent grain refiner, which is more economical in use. A further advantage is that the filters used during casting last longer. Without wishing to be bound to any theory in this respect, it is believed that the preparation of a grain refiner starting from AlB_{12} involves a different reaction kinetics, resulting in smaller borides and intermetallic compounds. The fact that less grain refiner is required, offers two advantages when recycling aluminium. For many applications a high titanium content
25 adversely affects the quality of the cast aluminium products. As a consequence of the fact that less grain refiner according to the invention is required, there is a minimal change in the composition of the aluminium melt and thus the expected material properties. In addition, such a
30 small increase also allows the aluminium to be recycled more often.

According to a preferred embodiment, the prepared grain refiner is subjected to an extrusion process before being contacted with the aluminium melt.

- 35 This makes it possible to produce a grain refiner with further improved grain-refining properties.

The invention further relates to a method of casting aluminium products, wherein an Al-Ti-B grain refiner is added to an aluminium melt.

This method is characterized by the addition of a grain refiner prepared according to the invention.

Due to the fine grain structure a product prepared by this method possesses improved properties in respect of strength and ductility. This means that it can be embodied to be stronger and/or lighter. In addition, this method requires less grain refiner, thereby limiting wear on the filters that are used during the casting process.

Boron may partly or completely be replaced by carbon or a carbon compound comprising Al, Ti or B. In order to produce sufficient heat, usually at the most only a part of the reactants will be used in the form of an alloy or intermetallic compound; and for the sake of convenience, for example, at the most one alloy or intermetallic compound will be used. A suitable basis is at least 20% titanium in the form of metallic titanium, preferably at least 40%.

The invention will now be elucidated with reference to an exemplary embodiment.

Preparation of a grain refiner

For the preparation of a grain refiner according to the present invention 15.86 g Al, 7.50 g Ti and 1.82 g AlB_{12} , each in powder form, are mixed. The powder sizes of the starting substances were:

Al powder ("Type 1" Metalloys Ltd. (Sheffield, U.K.)): < 45 μm ;

Ti powder ("MP-020" Micron Metals Inc. (Utah, USA)): < 45 μm ;

AlB_{12} powder (Grade "A" H.C. Starck GmbH & Co. KG (Goslar, Germany)): < 3 μm .

After mixing, the powder mixture is compressed at a pressure sufficiently high to form a solid body. Subsequently the solid body is placed into a furnace and heated under an argon atmosphere, wherein the furnace temperature is raised at a rate of 20°C/min. Once it has been established, with the aid of a temperature sensor provided in the furnace, that an exothermic reaction is taking place in the solid body, heating is discontinued. After being allowed to cool in the furnace and still under an argon

atmosphere, the grain refiner is ready for use. Boron may partly or completely be replaced by carbon.

Test of the grain refiner

The grain refiner obtained as above was tested by
5 examining its effect on the casting structure of the aluminium melt. The composition of the aluminium melt was Fe: 0.16% by weight; Si: 0.05% by weight; Sn, Pb, Zn, Cu, Ni, Mn, Cr, Ti, Mg < 0.01% by weight. When the temperature of the aluminium melt was 750°C, grain refiner was added in
10 an amount to correspond to 0.03% by weight of titanium in relation to the final aluminium melt. The mixture was subsequently stirred manually for 15 seconds. Within 30 seconds after stirring had ceased, a sample was cast in a preheated sand mould having a temperature of 50°. After
15 the first cast the temperature of the aluminium melt was maintained at 740°C and after 8 hours and 24 hours, more samples were cast; also at a temperature of 740°C.

The mean grain size was determined by etching a casting structure with aqua regia (25% HNO₃ + 75% HCL) and
20 by using the line interception method known in the art. In this method the frequency of a line passing the grain boundary is measured. The relation between the length of the line and the number of grain boundaries measured give the mean size of the grain. The results are given in the
25 table below.

TABLE

		grain size
30	20 sec.	200 µm
	8 hours	165 µm
	24 hours	140 µm

Control experiment

The following control experiment was carried out
35 using the data from the American patent specification 4,710,348, claiming that the mixture described therein is suitable as grain refiner for aluminium.

A powder mixture of aluminium, titanium and boron, whose composition was the same as described above, was

compressed into a solid body. The solid body was added to an aluminium melt under the same conditions as described above but without heating the solid body under an inert atmosphere in a furnace. No grain refinement was observed.

CLAIMS

1. A method of preparing an Al-Ti-B grain refiner for cast aluminium-comprising products, which grain refiner is prepared by:

- 5 i) mixing powders selected from the group comprising aluminium, titanium, boron, and alloys and intermetallic compounds thereof;
- ii) compressing the mixed powders;
- iii) heating the compressed mixture; and
- 10 iv) cooling the thus prepared grain refiner, characterized in that the compressed mixture is heated in an inert environment to initiate an exothermic reaction.

2. A method according to claim 1, characterized in that the reaction parameters are adjusted such that the ratio of elongated and cubic Al_3Ti crystals is as low as possible.

3. A method according to claim 1 or 2, characterized in that the ratio is changed by choosing the mole ratio of B/Ti such that it is lower than 1.9, in particular lower than 1.7, and more preferably lower than 1.5.

20 4. A method according to one of the preceding claims, characterized in that the size of the powders used in step i) is preferably less than 100 μm .

5. A method according to one of the preceding claims, characterized in that the prepared grain refiner is subjected to an extrusion process before being contacted with the aluminium melt.

6. A method according to one of the preceding claims, characterized in that the mixture from step i) preferably comprises titanium in an amount of at least 15% by weight and more preferably at least 25% by weight.

30 7. A method according to one of the preceding claims, characterized in that the mixture from step i) comprises boron in an amount of at least 3% by weight and more preferably at least 5% by weight.

8. A method according to one of the preceding claims, characterized in that in the preparation of the grain refiner, AlB_{12} is used as the boron source.

5 9. A method of casting aluminium products, wherein an Al-Ti-B grain refiner is added to an aluminium melt, characterized in that a grain refiner prepared according to one of the claims 1 to 8 is added.

INTERNATIONAL SEARCH REPORT

International Application No
PC 1/NL 99/00328

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22C1/03 B22F3/23

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C22C B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 521 580 A (SHELL INT RESEARCH) 7 January 1993 (1993-01-07) cited in the application page 2, line 53 - page 3, line 32; claims 1-12	1-9
X	GB 2 299 099 A (MAYES CHRISTOPHER DUNCAN) 25 September 1996 (1996-09-25) cited in the application page 4, line 25 - page 5, line 1; claims 1,7	1,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0521580	A	07-01-1993	AU 1943892 A JP 5195108 A	07-01-1993 03-08-1993
GB 2299099	A	25-09-1996	NONE	